

Warder (Robt. B.)

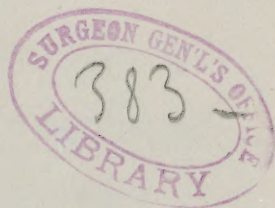
Examination of Commercial Black Antimony,
Tartar Emetic, and Glycerin.

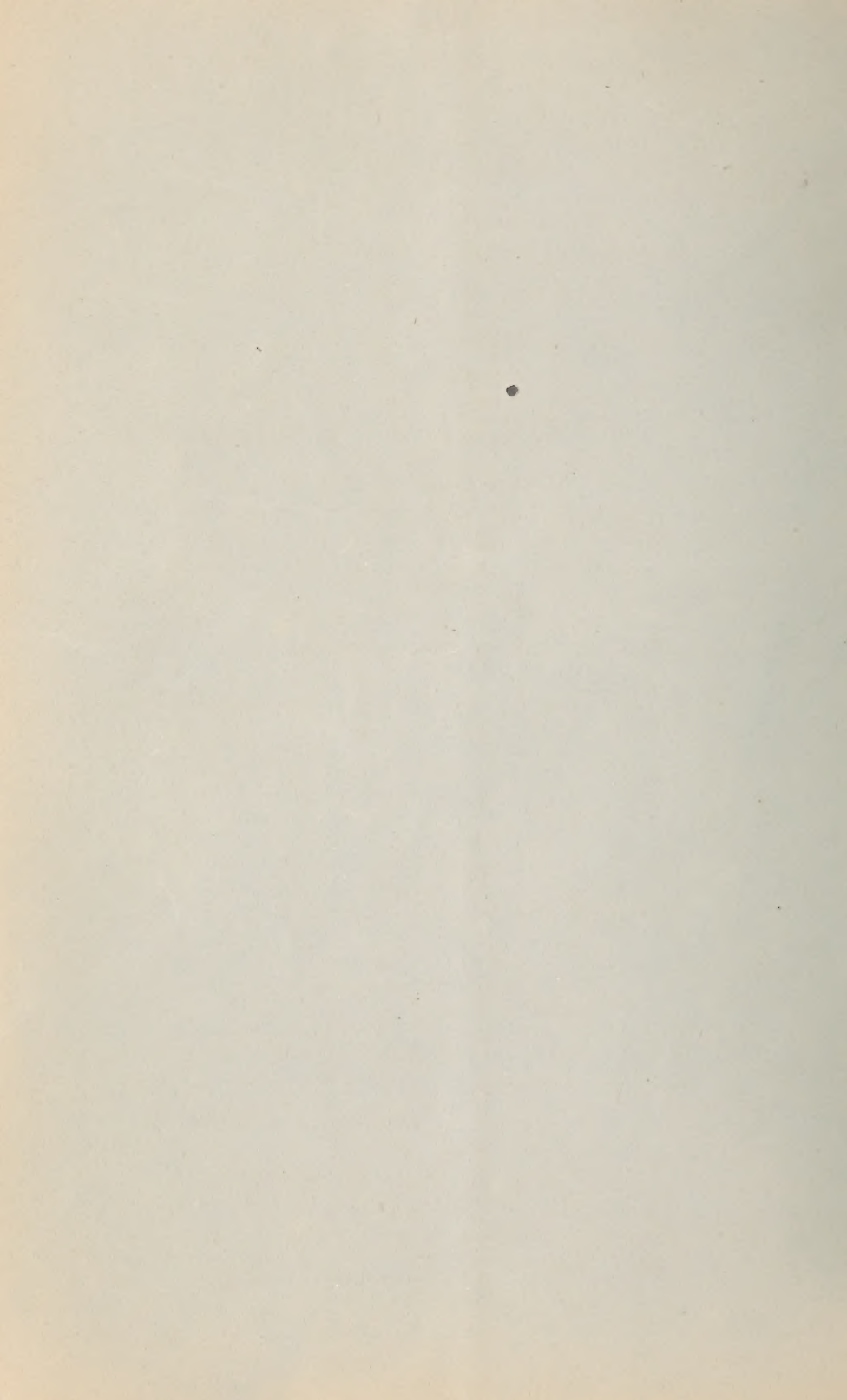
Papers presented to the 33d Annual Meeting of
the American Pharmaceutical Association, at
Pittsburgh, Pa., September, 1885.

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BLACK ANTIMONY OF COMMERCE.*

BY ROBERT B. WARDER.

QUERY No. 84.—*What is black antimony of commerce?*

The term "black antimony" is sometimes applied to the powdered metal, as in Roscoe & Schorlemmer's Treatise on Chemistry, Vol. II., part ii., p. 306; but in pharmacy it is supposed to mean the powdered stibnite or native sulphide.

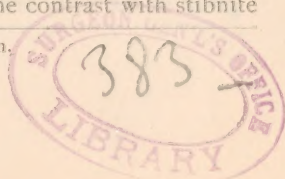
Fifteen samples were procured from as many retail druggists in eastern cities and the central states; and it soon became evident that the name is used in very different senses in the two sections of the country. The "pure antimony black" of the price lists is the genuine stibnite in a powdered form—there is no evidence that it has been purified; "commercial antimony black," on the other hand, is an utterly spurious imitation of the same, yielding no trace of antimony by the tests of the Pharmacopœia.

The following table shows the localities where the several samples were procured, and the reaction of the two kinds:

1. Cincinnati, Ohio.	{	HCl dissolved a portion of each sample (usually with violent effervescence in the cold), leaving considerable black residue. There was no evolution of H_2S , and no traces of antimony could be detected in the solutions by means of water or H_2S . Specific gravity of the powder, including air spaces, about 1.25.
2. " "		
3. Chicago, Ill.		
4. " "		
5. Ypsilanti, Mich.		
6. Indianapolis, Ind.		
7. Lafayette, Ind.		
8. Vincennes, Ind.		
9. " "		
10. Boston, Mass.	{	HCl dissolved each sample (except a small residue), with moderate effervescence of H_2S . Each solution gave a heavy white precipitate by dilution with water, soluble in tartaric acid. H_2S re-precipitated orange Sb_2S_3 .
11. " "		
12. New York, N. Y.		
13. Philadelphia, Pa.		
14. " "		
15. " "		

The appearance of these two substances is different enough when seen side by side, especially when observed with a lens. Powdered stibnite (Nos. 10 to 15) is inclined toward a bluish red color, with almost metallic lustre, suggestive of ground galena. No. 14 was very finely powdered, and appeared less lustrous unless pressed with a knife blade. Nos. 1 to 9 have a duller appearance of iron grey: the contrast with stibnite

* Presented at the Fourth Session.



gives the impression of a reddish tinge. With a pocket lens, however, the larger particles shine with a black resinous lustre like anthracite coal. No. 1 was unchanged by heating in a closed tube, and effervesced in the cold with HCl, leaving a black residue that burned with difficulty to a whitish ash. The acid solution contained both calcium and magnesium. A partial separation was made by simple elutriation, the black particles being washed off, while a white translucent powder was left. This effervesced with cold dilute HCl, and dissolved almost entirely on boiling. Sample No. 1 seems to have been made by mixing powdered anthracite with marble or magnesium limestone. Detailed analyses were not made of the remaining samples, except as indicated in the foregoing table; but they are all essentially like No. 1. Paper moistened with solution of lead acetate was used in each case, to test for traces of hydrogen sulphide. A bottle holding one ounce of water will hold $2\frac{1}{4}$ ounces of powdered stibnite (when well shaken together without pressure), but only $1\frac{1}{4}$ ounces of the imitation. This may afford a convenient mode of distinguishing between them, for those who do not wish to apply the chemical tests. In fact, the difference of specific gravity is so great, that any one accustomed to handle packages of such drugs would instantly suspect the spurious article from its greater bulk. A certain dealer is said to have defended his sales of the coal dust on the ground that genuine black antimony "kill all the stock in the country."

It is not the purpose of this paper to discuss moral questions; but it would be a great convenience to avoid ambiguity by calling coal and limestone by their own names.

TARTAR EMETIC OF COMMERCE.*

BY ROBT. B. WARDER.

QUERY NO. 68.—*What is the quality of commercial tartar emetic?*

Thirteen samples were procured from as many retail druggists in various cities. The ready solubility in water indicated the absence of notable quantities of acid potassium tartrate; but two specimens left a pulverulent residue, probably of antimonious oxide. Eight specimens contained at least traces of calcium, but only one contained traces of sulphate, while chlorides and iron were wholly absent, and any possible traces of arsenic were too small to be shown by Fleitman's test.

This drug is usually nearly pure, calcium salt being the chief impurity. This could easily be introduced with the acid potassium tartrate used in manufacture, and would seldom lead to injurious results. Details are given in the table below:

* Presented at the Fourth Session.

No.	Locality.	Action with water.	With Am_2O_3 .	With BaCl_2 and HCl .	No indication in any of the samples of chlorides with AgNO_3 , of iron, etc., with K_4Fdy , nor of arsenic by Fleitman's test.
1	Cincinnati, O. . .	Soluble.	Precipitate on standing.	Clear.	
2	Chicago, Ill. . . .	Soluble.	Clear.	Clear.	
3	" . . .	White residue.	Precipitate.	Clear.	
4	Ypsilanti, Mich. .	Soluble.	Precipitate.	Clear.	
5	Indianapolis, Ind.	White residue.	Precipitate.	Clear.	
6	Lafayette, Ind. . .	Soluble.	Precipitate.	Clear.	
7	Vincennes, Ind. .	Soluble.	Marked precipitate.	Slight precipitate.	
8	Vincennes, Ind. .	Soluble.	Clear.	Clear.	
9	Boston, Mass. . .	Soluble.	Slight precipitate.	Clear.	
10	Boston, Mass. . .	Soluble.	Clear.	Clear.	
11	New York, N. Y.	Soluble.	Clear.	Clear.	
12	Philadelphia, Pa .	Soluble.	Marked precipitate.	Clear.	
13	Philadelphia, Pa .	Soluble.	Clear.	Clear.	

GLYCERIN OF COMMERCE.*

BY ROBT. B. WARDER.

QUERY No. 34.—*How does the glycerin of commerce conform to the requirements of the Pharmacopœia?*

While the following paper was suggested by the query named, the products of the principal American manufacturers have also been compared with each other and with samples from retail druggists of a few central cities. The French and German goods sold in the East have not been included, except, perhaps, in a single sample, No. 18, which was labeled "Sarg's C. P. glycerin."

SAMPLES.

Nos. 1-12 represent the manufacturers, and were all procured from original packages in the hands of wholesale dealers, except No. 2 and No. 10; these brands are in less frequent use than the rest, and samples were procured from the manufacturers, to save the expressage from distant places. No. 12 is a standard English brand, included for comparison. No. 3 and No. 12 are sold in pound bottles, at a much higher rate than most of the rest, which are sold in cans or casks. Nos. 13-20 were procured from retail druggists. Every effort was made to have perfectly clean and dry bottles; but circumstances did not allow me to see to this personally in every case.

* Presented at the Fourth Session.

COLOR, ODOR, AND NEUTRALITY.

Each sample was a colorless, viscid liquid, except No. 4, which had a pale straw color.

No odor was observed in the cold except in a single sample, which had the disagreeable, candle-like odor of crude glycerine. Personal observation convinces me that the same brand is not usually so contaminated.

When heated on the water-bath, with the addition of half a volume of water,* odors were observed in seven other samples—two of them were very slight. The retail samples averaged better in this respect than those representing the manufacturers.

No butyric or other acidulous odors were developed by warming with an equal volume of dilute sulphuric acid.

Very faint acid reaction was observed in some specimens after dilution with $\frac{1}{2}$ volume of water, but not sufficient in any case to redden litmus paper that was distinctly blue. Negative results were also obtained (after dilution with ten volumes of water) with blue paper slightly inclined to purple. A purple paper should have been prepared for the purpose, but this was omitted till it was too late.

SPECIFIC GRAVITY.

The densities were determined by a specific gravity bottle, upon an accurate balance. Temperatures were noted (from 23.6° to 28.1° C.) and the density was calculated in each case for 15.5° C. by adding 0.0054 to the density found, for each degree Centigrade. The results are given in the table appended, and refer to the density of water at 4° C. It will be seen that only four samples are fully equal to the requirements of the Pharmacopœia, while Mr. Kennedy's determinations as reported to the Pennsylvania Pharmaceutical Association in 1884, showed very little deficiency in this respect. The bottles were all kept tightly corked until the determinations were made; and although Nos. 1–15 were examined on a damp day, the neck of the bottle used was large enough to allow of prompt filling and discharge, and the moisture absorbed during manipulation must have been inconsiderable.†

The bottle was carefully tested with distilled water. Reference to water at 15.5° C. instead of the maximum density, with the most liberal probable correction for the temperature of the glycerin, would scarcely add 0.002 to the densities reported. This margin of allowance would bring the majority within the limit 1.250; if the retail samples are diluted by five-tenths of one per cent. of water beyond the standard, this is as likely to arise from unavoidable circumstances as from intent or careless-

* Mr. Kennedy recommends heating with the addition of water, but this is not required in the Pharmacopœia. See "Proc. Penna. Pharm. Assoc." for 1884, p. 136.

† Mr. Kennedy found that glycerine of 1.26 spec. grav. exposed to the atmosphere in an open flat jar absorbed 7% of moisture in seven days.—*Proc. Amer. Pharm. Assoc.*, for 1879, p. 726.

ness. Nos. 9 and 10 are not so high as we would expect from the claims of the makers.

ACRYLIC ACID, ETC.

Special importance is attached by manufacturers to the test with silver nitrate for acrylic acid and similar impurities, arising from a partial decomposition of fats. The Pharmacopœia states that there should be "no coloration," without specifying the time of action, nor the amount of exposure to light. Much care is required to secure absolute cleanliness in applying this test, as even traces of insensible perspiration from the fingers may invalidate the result. Twenty-two 2-drachm bottles with glass stoppers were accordingly very thoroughly washed; the lip of each sample bottle was carefully wiped with paper and then rinsed with a portion of the glycerin itself to be thrown away, before pouring into the test bottles. The latter were filled one-eighth full with the several samples; they were then filled half full with distilled water and well shaken, in order to diminish the viscosity, and facilitate the final mixing with the reagent. Each bottle was nearly filled with a five per cent. solution of silver nitrate, well shaken, and placed on white paper with uniform exposure to diffused light. The bottles were taken in order as numbered, and the last was in place five minutes after No. 1 had received the silver solution. Care was then taken to secure uniformity in the conditions.

The last two test bottles were filled with silver nitrate and distilled water for purposes of comparison. The bottles were observed from time to time during five hours' exposure to ordinary daylight; afterward they were kept in the dark, and observed at intervals for fifteen days. The more important changes are noted in the table. There was no immediate change of color in any sample; the promptness and speed of the deepening of color and formation of precipitate varied greatly. The observations could have been rendered more accurate by providing a series of standard colors in similar bottles from permanent materials, with which to compare the silver solutions reduced by the glycerin from time to time. The terms used must be understood to be relative merely, for the manufacture of glycerin in this country has been brought to such a degree of perfection that what would usually be called a very slight reaction is recognized in this test as a distinct color. A reddish or violet test usually appeared after a longer or shorter time, changing to gray as the precipitates began to form. The only appearance of a distinct lead gray in No. 8 was quite exceptional. The several samples did not maintain the same order of discoloration when observed at different times. Thus, after one or two hours, No. 12 was less limpid than No. 6; but after five hours the former seemed unchanged, while No. 6 was decidedly deeper. The amount of light present also has a very great influence; one test exposed near a window to diffused light from the clear sky became about as dark in twenty minutes as a duplicate test which had been

prepared two hours before, and which faced the interior of a well-lighted room, but was protected from the direct glare of the windows. No. 4 had a decided precipitate after three hours; No. 10 had a smaller amount at the same time. Three samples only showed precipitate on the day of mixing; seventeen contained solid particles after three days; No. 12 alone was free from precipitate after ten days, and a few little specks were seen in this after fifteen days. The blank test containing silver nitrate and distilled water remained perfectly limpid for ten days, and showed only the slightest discoloration at the time of the last observation. This precaution was deemed needful to demonstrate the purity of the water used. The table shows considerable variation among the several brands, but no manufacturer should be condemned for the results of these experiments with single samples. Considerable variations among samples of the same brand have been noted. The requirements of the Pharmacopœia should be more definitely stated in the next revision; and if there should be sufficient demand for the utmost possible purity, an investigation should be made to determine the conditions needful to secure constant results—especially the influence of light, time, and excess of silver nitrate. With the present reading of the Pharmacopœia, probably not more than one of the samples would be condemned, as the analyst does not usually think needful to wait more than a few minutes for a reaction to take place. The retail samples average quite as well as those representing manufacturers.

WHOLESALE DRUGGISTS.

No.	Specific gravity.	Color and precipitate with AgNO_3 after					
		$\frac{1}{2}$ hour.	1 hour.	2 hours.	5 hours.	3 days.	10 days.
1	1.248	I	3	4	4	C	E
2	1.250	I	3	3	3	B	B
3	1.247	I	3	4	4	C	D
4	1.248	4	5	7	B	E	F
5	1.253	I	3	4	4	C	E
6	1.249	I	I	I	3	B	B
7	1.249	I	I	I	2	A	B
8	1.253	I	4	6	6	C	D
9	1.229	I	3	4	4	C	F
10	1.244	2	4	7	B	E	F
11	1.258	I	2	3	3	A	D
12	1.248	I	2	2	2	A	A

RETAIL DRUGGISTS.

13	1.249	I	I	2	3	C	F
14	1.246	I	2	2	3	B	C
15	1.248	I	3	3	3	B	C
16	1.246	I	4	4	4	B	B
17	1.247	2	4	4	4	C	D
18	1.246	2	4	7	B	E	F
19	1.248	I	3	4	4	C	F
20	1.246	I	2	3	3	B	C

Color.	Explanation.	Precipitate.
1. None.		A. None.
2. Almost clear.		B. Very slight.
3. Very pale.		C. Slight.
4. Pale tinge.		D. Medium.
5. Pale violet.		E. Considerable.
6. Grey.		F. Heavy.
7. Distinct violet.		

TESTS FOR SUGARS, ETC.

1. *Evaporation Test.* The Pharmacopœia requires that not more than a black stain shall remain when about two grams of the glycerin are heated to boiling in a small capsule on the sand-bath, and then ignited, while sugar leaves a porous coal. It may be assumed that the lamp is to be removed when the vapors are ignited, but this is not expressly stated. Variations in the intensity of the heat led to some misleading results, and the following plan was finally adopted: About two grams of glycerin were poured into a small platinum crucible, which was placed in an inclined position (to facilitate access of air) deep in the sand-bath. When the liquid began to boil, the vapors were ignited and the lamp removed. The liquid then burned away to the last drop. Comparative tests were made with glycerin containing one-half per cent. of sugar, added as syrup to insure solution. In this case a considerable mass of porous black residue was always left. The samples of glycerin nearly always left something more than a "black stain;" there were traces of porous substance of yellowish brown to dark color, which quickly swelled and carbonized when exposed to the flame. The volume of this residue before carbonization, even when most abundant, was judged to be about one-third as great as the residue left under like circumstances by the same quantity of glycerin containing 0.5% cane sugar.

2. *Sulphuric Acid Test.* The Pharmacopœia requires that glycerin shall not become dark colored when warmed with an equal bulk of concentrated sulphuric acid. Some preliminary experiments gave variations from a straw color to a deep amber with the same sample, on simply mixing the two fluids. Heating on the flame resulted in carbonization and frothing. Comparative tests were accordingly made with glycerin containing 0.5%, 1%, and 2% of cane sugar respectively; the first, when mixed with an equal volume of acid, became very dark colored, but was not quite opaque for some time. After a few hours it was black; the second and third tests became black and opaque at once.

Moderate variations in temperature may have marked influence upon the intensity of the reaction; and experiments were therefore made to see how much variation was likely to result from differences in the relative amounts of glycerin and acid. Ten cubic centimeters of each at 24° C.,

rose to 97° C., on being mixed, showing an increase of 73° from the reaction. Five cc. glycerin mixed with 10 cc. acid rose to 98° C. Ten cc. glycerin with 5 cc. acid rose to 91° C. It thus appears that considerable variations in the quantity of acid may produce little variation in the temperature, if the acid is in excess; but two liquids of such viscosity are liable to be imperfectly mixed in a test-tube, unless special care is taken. If an excess of acid remains in contact with the glycerin, it may first remove the water, and then begin a process of carbonization.

In several instances, where the liquids seemed to be thoroughly mixed, with the production of a straw color a darkening was observed near the bottom of the tube after some minutes, indicating that an excess of acid in that part had escaped thorough mixing. When no flame was applied to the mixture, a deep amber was the darkest color obtained; and this was characterized by strong fluorescence. The color in no case approached that produced immediately by glycerin No. 6 containing 0.5% of cane sugar. From these two tests we may safely conclude that no sugar or like materials had been added to any of the samples examined; but either the destructive distillation of pure glycerin or its dehydration with sulphuric acid may yield traces of substances of higher molecular weight very similar in deportment to sugar.

The use of Fehling's solution after prolonged boiling with acid, was considered superfluous for the object in view.

MINERAL IMPURITIES AND OXALIC ACID.

Diluted with ten volumes of water, each sample remained perfectly clear, with additions of barium chloride, calcium chloride, ammonium oxalate, and ammonium sulphide; sulphates, oxalates, calcium salts, and the heavy metals, are, therefore, absent. The residues left on evaporation were combustible, leaving no ash.

CONCLUSIONS.

The twenty samples tested conform very nearly to the requirements of the Pharmacopœia, though a very slight excess of moisture is indicated in several instances; one sample had a very disagreeable odor; one also had some color, and gave distinct reaction with silver nitrate within half an hour. The manufacturers maintain a high standard of excellences; and retailers, so far as observed, do not adulterate the goods in their stores. It should be mentioned in this connection, however, that adulterations are not unknown in the east. Cane sugar seems to be generally used for this purpose, since glucose is very readily detected by Fehling's solution.

ACKNOWLEDGMENT.

My sincere thanks are due to Prof. J. U. Lloyd, for many suggestions during the course of this investigation.

